Influence of sulfur on the fate of heavy metals during clinkerization

Bin Zhang¹, Anna Bogush², Jiangxiong Wei¹,³*, Tongsheng Zhang¹,³, Weiting Xu¹,³, Qijun Yu¹,³

1. School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, Guangdong, China
2. Centre for Resource Efficiency & the Environment (CREE), Department of Civil, Environmental & Geomatic Engineering (CEGE), University College London (UCL), Chadwick Building, Gower Street, London WC1E 6BT, UK
3. Guangdong Low Carbon Technologies Engineering Center for Building Materials, Guangzhou 510640, Guangdong, China

ABSTRACT

The fate of heavy metals during clinkerization is of crucial significance to the solid waste utilization, environmental management, and sustainable development. This paper presents a laboratory scale simulation that aims to investigate the effects of sulfur on the fate of Cu, Pb, and Cd during clinkerization. The sulfur-bearing phases (CaSO₄·2H₂O and CaS) and metal oxides were mixed with cement raw meal in appropriate ratios to produce clinkers. The volatilization and solidification of Cu, Pb and Cd were investigated using atomic absorption spectrometry, thermogravimetric

* Corresponding author: jxwei@scut.edu.cn, Tel.: +86 020 8711 4137
analysis, X-ray diffraction analyses, electron probe X-ray microanalysis, and scanning electron microscopy. The volatilization of Cu slightly increased in the temperature range 950°C - 1450°C with addition of sulfur. Sulfur promotes the volatilization of Pb and Cd at the temperature from 950°C to 1250°C by decreasing the melting point of PbO and CdO. Sulfur increased the solidification ability of clinker decreasing the volatilization ratio of Pb and Cd at the temperature of 1350-1450°C and 1450°C, respectively. Both forms of sulfur (CaSO₄·2H₂O and CaS) have similar effect on the Cu/Pb/Cd volatilization. Sulfur concentrated in interstitial phases of the clinkers mainly as Ca₄Al₆O₁₂SO₄ and CaSO₄. Cu, Pb and Cd were mainly solidified within interstitial phases of the clinkers forming solid solutions with the variable compositions. Cu was also present in alite and belite and as crystalline phases of Ca₂CuO₃ and CaCu₂O₃ in the clinkers. This research can help to improve understanding of the fate of heavy metals and provide a guideline for risk assessment during the co-processing of solid wastes in cement kiln.

Keywords: clinker, heavy metals, sulfur, volatilization, solidification, element speciation

1. Introduction

Due to the rapid development of modern industry and city, significant amount of solid wastes (SW) are being produced every day, for instance, 3.28 billion tons of industrial SW, 173 million tons of municipal solid waste (MSW) and 25 million tons of
sludge were produced in China in 2016 [1]. About 77% of the solid wastes were transported to the landfills and waste incineration facilities [2]. However, solid wastes can be considered as secondary raw fuels and/or materials in the cement industry, for example, in co-processing of solid wastes in the cement kiln [3-6]. By the implementation of co-processing, the natural resources can be saved and carbon dioxide emissions can be reduced [7-10]. Nevertheless, most of the solid wastes contain heavy metals that could be volatilized and move with flue gas into the atmosphere during clinkerization, polluting the environment and threatening human health [11-13]. Therefore, it is important to study the volatilization of heavy metals during co-processing of solid wastes in the cement kiln.

The previous studies carried on heavy metal emissions from solid wastes co-processing indicated that the fate of heavy metals strongly depended on the waste composition, particularly on the content of chlorine and sulfur in the solid wastes and cement raw meal [14, 15]. The content of sulfur in the cement kiln is about 0.5 wt.% to 2.0 wt.%, that mainly come from raw fuels (e.g., coal) and materials (e.g., limestone containing sulfide minerals) combustion [16]. The content of sulfur in the cement kiln might increase due to co-processing of solid wastes with high content of sulfur. Therefore, the detailed investigation of the effect of sulfur on the fate of heavy metals in co-processing of solid wastes in the cement kiln are required. Chan et al. [17], Smith [18], and Nowak et al. [19, 20] focused on the effect of sulfur (such as Na₂SO₄ and K₂SO₄) on the volatilization of heavy metals during the burning of solid wastes. However, the temperatures investigated were relatively low (<1200°C) comparing to the
Portland cement clinker production (T=1450°C). Moreover, cations from the sulfates such as Na\(^+\) and K\(^+\) might influence on the clinkering process, volatilization and solidification of heavy metals [21, 22].

Heavy metals like Cu, Pb, and Cd commonly exist in the solid wastes such as Pb-Zn slag, residues from MSW incineration facilities and sewage sludge [23-25]. Heavy metals might volatilize and move with flue gas into the atmosphere. Pb and Cd are easy to volatilize during the thermal treatment process of solid wastes [17, 20, 26-27]. CuO is known to act as flux and/or mineralizer in the clinkerization because it decreases the melting temperature considerably and favours the combination of free lime [20, 28].

In this research, the effects of sulfur on the fate of Cu, Pb, and Cd was emphasized and the binary system of clinker-heavy metal in the study of co-processing of SW in cement kiln was developed to ternary system of clinker-heavy metal-sulfur, which is more coincident with the condition of co-processing of SW in cement kiln. Two sources of sulfur as gypsum (CaSO\(_4\)·2H\(_2\)O) and calcium sulfide (CaS) were used in our experiments. The relationships among sulfur sources, volatilization and solidification of Cu/Pb/Cd, and mineral phases of clinker were investigated. This paper can help to improve understanding of the fate of heavy metals in presence of sulfur and provide a guideline for risk assessment during the utilization of solid wastes in cement kiln.

2. Materials and method

2.1. Materials

Cement raw materials such as CaCO\(_3\), SiO\(_2\), Al\(_2\)O\(_3\), and Fe\(_2\)O\(_3\), were supplied by
pure chemical reagent in order to eliminate the effects of impurity ions such as Na\(^+\), K\(^+\), and Cl\(^-\) in the industrial raw materials. Cu, Pb, and Cd were added to the raw mixes as CuO, PbO and CdO, respectively. S was added in two different species as sulfate (gypsum - CaSO\(_4\cdot2\)H\(_2\)O) and sulfide (CaS).

2.2. Experimental procedure

The phase composition of cement clinkers was controlled by Bogue method (see Eq. (1) – (3)) [28]. Lime saturation ratio (KH), silica ratio (SM), and alumina ratio (IM) were designed as 0.9, 2.5, and 1.6, respectively. The theoretical mineral composition was calculated to be 56% of alite (C\(_3\)S), 20% of belite (C\(_2\)S), 8.6% of aluminate (C\(_3\)A), and 10% of ferrite (C\(_4\)AF). Cement raw meals with 2.0 wt.% of Cu, Pb, or Cd were prepared and sulfur concentration was varied (0.5 wt.%, 1.0 wt.%, 1.5 wt.%, and 2.0 wt.%). Table 1 lists the formulated mixtures.

\[
\text{Lime saturation ratio (KH)} = \frac{CaO - 1.65Al_2O_3 - 0.35Fe_2O_3}{2.8SiO_2}
\] (1)

\[
\text{Silica ratio (SM)} = \frac{SiO_2}{Al_2O_3 + Fe_2O_3}
\] (2)

\[
\text{Alumina ratio (IM)} = \frac{Al_2O_3}{Fe_2O_3}
\] (3)

Table 1

<table>
<thead>
<tr>
<th>ID.</th>
<th>Cu</th>
<th>Pb</th>
<th>Cd</th>
<th>CaSO(_4\cdot2)H(_2)O/CaS (S: wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(_{Cu-S-0})</td>
<td>2.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>S(<em>{Cu-CaSO4-0.5}/S</em>{Cu-CaS-0.5})</td>
<td>2.0</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>S(<em>{Cu-CaSO4-1.0}/S</em>{Cu-CaS-1.0})</td>
<td>2.0</td>
<td>0</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>S(<em>{Cu-CaSO4-1.5}/S</em>{Cu-CaS-1.5})</td>
<td>2.0</td>
<td>0</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>$S_{\text{Cu-CaSO}<em>4-2.0}/S</em>{\text{Cu-CaS}-2.0}$</td>
<td>2.0</td>
<td>0</td>
<td>0</td>
<td>2.0</td>
</tr>
<tr>
<td>-----------------------------------------</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>$S_{\text{Pb-S-0}}$</td>
<td>0</td>
<td>2.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$S_{\text{Pb-CaSO}<em>4-0.5}/S</em>{\text{Pb-CaS}-0.5}$</td>
<td>0</td>
<td>2.0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>$S_{\text{Pb-CaSO}<em>4-1.0}/S</em>{\text{Pb-CaS}-1.0}$</td>
<td>0</td>
<td>2.0</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>$S_{\text{Pb-CaSO}<em>4-1.5}/S</em>{\text{Pb-CaS}-1.5}$</td>
<td>0</td>
<td>2.0</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>$S_{\text{Pb-CaSO}<em>4-2.0}/S</em>{\text{Pb-CaS}-2.0}$</td>
<td>0</td>
<td>2.0</td>
<td>0</td>
<td>2.0</td>
</tr>
<tr>
<td>$S_{\text{Cd-S-0}}$</td>
<td>0</td>
<td>0</td>
<td>2.0</td>
<td>0</td>
</tr>
<tr>
<td>$S_{\text{Cd-CaSO}<em>4-0.5}/S</em>{\text{Cd-CaS}-0.5}$</td>
<td>0</td>
<td>0</td>
<td>2.0</td>
<td>0.5</td>
</tr>
<tr>
<td>$S_{\text{Cd-CaSO}<em>4-1.0}/S</em>{\text{Cd-CaS}-1.0}$</td>
<td>0</td>
<td>0</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$S_{\text{Cd-CaSO}<em>4-1.5}/S</em>{\text{Cd-CaS}-1.5}$</td>
<td>0</td>
<td>0</td>
<td>2.0</td>
<td>1.5</td>
</tr>
<tr>
<td>$S_{\text{Cd-CaSO}<em>4-2.0}/S</em>{\text{Cd-CaS}-2.0}$</td>
<td>0</td>
<td>0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

The formulated mixtures were thoroughly blended and homogenized in a mechanical planetary mixer. Then each mixture was mixed with 8% of absolute ethanol and pelletized into Ø10×50 mm cylindrical bar under 40 MPa. Each pellet was calcined from room temperature to the designated temperature at a heating rate of 10 °C/min. When the furnace reached designated temperature, it was maintained for 45 min and then the clinkers were cooled quickly in air to the room temperature [28].

2.3. Analytical methods

The clinkers were grounded into fine powder. The clinker samples were dissolved using an acid mixture of hydrogen peroxide ($\text{H}_2\text{O}_2$), aqua regia, and hydrogen fluoride (HF) in a volume ratio of 2:5:2 in a microwave digestion system (ZEROM, China). The concentrations of Cu, Pb and Cd in the solutions were analyzed by flame atomic absorption spectrometry (AAS, Analytik Jena AG, Germany). The duplicate measurements were carried out, and the average values were used to calculate the volatilization percentage according to Eq. (4):
\[ H = \left(1 - \frac{K}{S/(1 - \text{LOI})}\right) \times 100\% \]  

(4)

Where, \( H \) is the volatilization ratio of Cu, Pb or Cd; \( K \) (mg/kg) is the content of Cu, Pb or Cd in the clinker; \( S \) (mg/kg) is the content of Cu, Pb or Cd in raw materials; and LOI represents the loss on ignition.

The distribution of Cu, Pb and Cd in the clinker phases was investigated on the polished sections by electron probe micro-analysis (EPMA-1600, Shimadzu, Japan). The measurement was conducted with an acceleration voltage of 15.0 kV and an electron beam diameter of 1μm. The morphology of the clinkers and element analyses were investigated by scanning electron microscopy (SEM, EVO 18, Carl Zeiss, Germany) equipped with energy-dispersive X-ray spectroscopy (EDS, Oxford Instrument INCAx-sigth EDS-system). SEM/EDS analyses were performed with a 20 kV accelerating voltage.

Thermogravimetric analysis (TG) was used to investigate the influence of sulfur on the volatilization temperature of heavy metals. TG curves were obtained using a NETZSCH STA 449F3 instrument. TG analysis was conducted using about 20 mg of sample (chemical reagent) in alumina pans with an air purge gas flow rate of 100 mL/min, equilibration at 30°C for 10-15 min, followed by a heating rate of 10°C/min from 30°C to 1250°C (for \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \) - up to 1400°C).

The mineralogical compositions of the samples were determined by X-ray diffraction analysis (Bruker D8). This diffractometer is equipped with Cu Kα (\( \lambda = 1.5406 \) Å, 40 kV and 40 mA). All patterns were scanned over the range \( 5^\circ < 2\theta < 70^\circ \) using a step size of 0.02° and a count time of 0.2 s.
Selective dissolution method was used to separate silicate and interstitial phases of the clinkers [29].

3. Results and discussion

3.1. Effect of sulfur and temperature on the volatilization of Cu, Pb, and Cd

Figure 1 to 3 show the results obtained for Cu, Pb, and Cd volatilization with the addition of CaSO_4·2H_2O and CaS at different temperatures. Without addition of sulfur, the volatilization ratio of Cu (Figure 1) increased from 6.0% to 20% with increasing the temperature from 950°C to 1450°C. However, the Cu volatilization slightly increased (~ 10%) with increasing sulfur content.

![Graph showing volatilization of Cu with sulfur addition](image)

**Fig. 1.** Volatilization of Cu with sulfur addition: a) CaSO_4·2H_2O; b) CaS.

Figure 2 shows that the volatilization ratio of Pb increased from 13.4% to 86.2% with increasing the temperature from 950°C to 1450°C without sulfur addition. The volatilization ratio of Pb slightly increased (~ 15%) with increasing CaSO_4·2H_2O content at the temperature of 950°C, 1050°C, 1150°C and 1250°C. However, when the temperature is higher than 1250°C, the volatilization ratio of Pb decreased with
increasing amount of CaSO₄·2H₂O. The significant decrease of Pb volatilization was observed at 1350°C (20.2%) and 1450°C (33.4%) with the addition of 2.0 wt.% of sulfur comparing to the reference sample.

![Fig. 2. Volatilization of Pb with sulfur addition: a) CaSO₄·2H₂O; b) CaS.](image)

The volatilization ratio of Cd increased from 23.9% to 59.4% with increasing the temperature from 950°C to 1450°C without sulfur addition (Figure 3). The volatilization ratio of Cd increased slightly (~ 12%) with increasing CaSO₄·2H₂O content at the temperature of 950°C, 1050°C, 1150°C, 1250°C and 1350°C. However, at the temperature of 1450°C, the volatilization ratio of Cd decreased by 21.9%, with the addition of 2.0 wt.% of sulfur, compared the reference sample.

![Fig. 3. Volatilization of Cd with sulfur addition: a) CaSO₄·2H₂O; b) CaS.](image)
Heavy metals were classified as volatile (Pb and Cd), semi-volatile (Zn, Sb, and Se), and non-volatile (Cr, Cu, Ni, As, Mn, and Co) elements [30]. Also, the melting and boiling temperatures of CuO (1026°C and 2000°C) are higher than that of PbO (888°C and 1535°C) and CdO (900°C and 1385°C), respectively. Therefore, Pb and Cd should have a higher volatilization ratio than Cu during clinkerization that was observed in our investigation. Sulfur in cement raw meal act as flux/mineralizer lowering the temperature of the liquid phase formation, increase the amount of the melt, and decrease the viscosity and the surface tension of the melt [31, 32]. Lowering the surface tension and the viscosity of the melt, normally formed at above 1338°C (an invariant point; [33]), can increase the diffusivity of the clinkering species (including Pb-bearing and Cd-bearing species) and therefore promote the solidification of Pb and Cd. According to Taylor [28, 34], Herfort et al. [35] and Wang et al. [36], sulfur dissolved in the melt can affect the acid-base equilibrium $[\text{MeO}_4]^{5-} \leftrightarrow [\text{MeO}_6]^{9-}$ of the amphoteric elements (Me: Al$^{3+}$ and Fe$^{3+}$). The displacement of this reaction to the left favors the formation of a network built from $[\text{MeO}_4]^{5-}$ and silicon tetrahedra that leads to the increase of the melt viscosity, while $[\text{MeO}_6]^{9-}$ is more mobile and promotes the decrease of the viscosity surface tension of the melt. These effects will promote the reaction among mineral phases and heavy metals. The more sulfur addition, the greater transformation degree of $[\text{MeO}_4]^{5-}$ to $[\text{MeO}_6]^{9-}$, and then the greater effect of sulfur on the volatilization/solidification of Pb and Cd will be observed. Therefore, the mineral phases of clinker might solidify more Pb and Cd, and their volatilization ratio decreased
when the temperature is higher than 1350°C, CuO is hard to volatilize and might act as flux/mineralizer itself. Therefore, the effect of sulfur on the Cu volatilization is not obvious.

Before the appearance of liquid phase during clinkerization (the temperature is lower than 1338°C), the effects of sulfur on the volatilization of heavy metals were caused by decreasing the volatilization temperature of heavy metals, that will be confirmed in Section 3.2.

It can be seen from Figure 1 (b) to Figure 3 (b) that the effect of CaS on the volatilization of Cu, Pb, and Cd is similar to that of CaSO\(_4\)·2H\(_2\)O. The reason is that CaS might be oxidized to CaSO\(_4\) at the temperature around 700°C [37, 38]. The chemical reactions (1) - (5) might occur during the process of oxidation. However, the equation (1) is the main oxidation reaction due to the lowest Gibbs free energy under 700°C (Figure 4) [37, 38]. During the preparation of clinker, most of CaS was oxidized to CaSO\(_4\) around 700°C and the mineral phases formation of clinker is higher than 1000°C. Besides, CaS is not reacting with heavy meal below the temperature of 700°C. Namely, the mechanism of the effects of CaS on the volatilization and solidification of Cu/Pb/Cd is the same as CaSO\(_4\).

\[
\begin{align*}
CaS + 2O_2(g) &= CaSO_4 \quad (1) \\
CaS + 3CaSO_4 &= 4CaO + 4SO_2(g) \quad (2) \\
CaS + 3/2O_2(g) &= CaO + SO_2(g) \quad (3) \\
CaO + 2SO_2 + 1/2O_2(g) &= CaSO_4 \quad (4) \\
CaS + 2SO_2 &= CaSO_4 + 2S \quad (5)
\end{align*}
\]
3.2. Effects of sulfur on the volatilization temperatures of Cu, Pb, and Cd

The results from thermogravimetric analysis are shown in Figure 5. The TG curves of gypsum showed the mass losses in the temperature range from around 150°C to 700°C due to dehydration of that mineral. Gypsum start decomposing at 1200°C. Cu, Pb, and Cd start volatilizing at 1015°C, 940°C, and 1070°C, respectively. The addition of corresponding content of sulfur leads to decrease the volatilization temperatures of Cu, Pb, and Cd by 40°C, 65°C, and 35°C, respectively. Therefore, the sulfur has a positive effect on the volatilization of Cu, Pb, and Cd at the temperatures <1250°C, that confirmed the results in Section 3.1. CaSO₄·2H₂O dehydrated at the temperature around 150°C and 700°C forming CaSO₄ and the most of CaS was oxidized to CaSO₄ around 700°C. CaSO₄ can act as mineralizer/flux changing the thermodynamic stability of CuO/PbO/CdO and, therefore, lowering their volatilization temperature.
Fig. 5. TG curves of CuO, PbO, or CdO with/without CaSO$_4$·2H$_2$O: a) CuO with/without CaSO$_4$·2H$_2$O; b) PbO with/without CaSO$_4$·2H$_2$O; c) Cd with/without CaSO$_4$·2H$_2$O.

3.3. Sulfur speciation in clinker

The XRD patterns of $S_{\text{Cu-CaSO}_4\cdot2\text{H}_2\text{O}}, S_{\text{Pb-CaSO}_4\cdot2\text{H}_2\text{O}}$, and $S_{\text{Cd-CaSO}_4\cdot2\text{H}_2\text{O}}$ samples sintered at 1450°C and their corresponding silicate and interstitial phases based on the selective dissolution method are shown in Figures 6-8. CaSO$_4$ (mainly for the S additions 1.5-2.0 wt.%) and Ca$_4$Al$_6$O$_{12}$SO$_4$, formed during clinkering process, were concentrated in the interstitial phases of the clinker. The content of C$_3$A and C$_4$AF in the clinker decreased but sulfoaluminate (Ca$_4$Al$_6$O$_{12}$SO$_4$) increased with increasing addition of sulfur. It was reported by Zhao [39] and Ma [40] that the calcium sulfoaluminate
(Ca₄Al₄O₁₂SO₄) was formed between the temperature of 1300°C and 1350°C in the system of CaCO₃-SiO₂-Al₂O₃-Fe₂O₃-CaSO₄. When the temperature is higher than 1350°C, Ca₄Al₄O₁₂SO₄ start to decompose to C₃A and CaSO₄. Therefore, the main speciation of sulfur in clinker were CaSO₄ and Ca₄Al₄O₁₂SO₄. Besides, the formation of Ca₄Al₄O₁₂SO₄ consumed some Al, which result in the decreased content of C₃A and C₄AF.

Fig. 6. XRD patterns of S_{Cu-CaSO₄-2.0} sample sintered at 1450°C: A) Clinker; B) Silicate phase; C) Interstitial phase.
Fig. 7. XRD patterns of S_{Pb-CaSO4-2.0} sample sintered at 1450°C: A) Clinker; B) Silicate phase; C) Interstitial phase.
Fig. 8. XRD patterns of $\text{SCd-CaSO}_4$ sample sintered at 1450°C: A) Clinker; B) Silicate phase; C) Interstitial phase.

3.4. Distribution of elements in the clinkers

3.4.1. EPMA analysis

The distribution of Si, Al, Cu, Pb, Cd and S in the clinkers are shown in Figures 9-11. Clinker consists of silicate phases ($\text{C}_3\text{S}$ and $\text{C}_2\text{S}$) and interstitial phases ($\text{C}_3\text{A}$ and $\text{C}_4\text{AF}$). It can be seen that the distributions of Cu, Pb, and Cd associated with Al in the clinkers. Therefore, Cu, Pb, and Cd were mainly solidified in interstitial phases of the clinker. The Cu, Pb, and Cd distributions in the clinker phases were not changed after the $\text{CaSO}_4\cdot2\text{H}_2\text{O}$ and CaS addition. According to the results from Section 3.3, interstitial phases mainly consist of $\text{C}_3\text{A}$, $\text{C}_4\text{AF}$ and $\text{Ca}_4\text{Al}_4\text{O}_{12}\text{SO}_4$ with the addition of 2.0 wt.% of S. During clinkerization, the interstitial phases gradually become liquid phase with temperature increasing. The addition of $\text{CaSO}_4\cdot2\text{H}_2\text{O}$ and CaS increased the amount of the melt and decreased viscosity and surface tension of the melt, accelerating migration of heavy metals in the liquid phase, promoting ion substitution and formation of solid solutions with heavy metals, and possibly the formation of new phases. The
substitution of $\text{Cu}^{2+}$, $\text{Pb}^{2+}$, and $\text{Cd}^{2+}$ for $\text{Al}^{3+}$ or $\text{Fe}^{3+}$ in $\text{C}_4\text{AF}$ and $\text{Al}^{3+}$ in $\text{C}_3\text{A}$ is possible. Also, formation of different solid solution by isomorphous replacement of $\text{Al}^{3+}$ or $\text{Fe}^{3+}$ ($\text{Al}^{3+}$ - ionic radius 0.39-0.54 and electronegativity 1.61; $\text{Fe}^{3+}$ - 0.63-0.92 and 1.83) by $\text{Cu}^{2+}$ (0.57-0.73 and 1.65), $\text{Pb}^{2+}$ (0.98-1.49 and 2.0), and $\text{Cd}^{2+}$ (0.78-1.31 and 1.93) is probable.

**Fig. 9.** An EPMA maps of the Si, Al, Cu, and S distributions in the clinkers: A) $\text{S}_{\text{Cu-S}}$-0.; B) $\text{S}_{\text{Cu-CaSO}_4}$-2.0; C) $\text{S}_{\text{Cu-CaS}}$-2.0.
**Fig. 10.** An EPMA maps of the Si, Al, Pb, and S distributions in the clinkers: A) $S_{\text{Pb-S}}$; B) $S_{\text{Pb-CaSO}_4-2.0}$; C) $S_{\text{Pb-CaS-2.0}}$. 
3.4.2. SEM/EDS analysis

The point chemical analysis of the polished clinker samples sintered at 1450°C was carried out to quantitatively investigate the content of Cu, Pb, and Cd in silicate and interstitial phases. About fifty spot-analyses were performed for each sample. The results are listed in Table 2. For the sample of $S_{Cu-S-0}$, the content of Cu is about 0.40 wt.% and 4.53 wt.% in silicate phases and interstitial phases, respectively. The addition of 2 wt.% sulfur as $CaSO_4 \cdot 2H_2O$ and $CaS$ had no effect on the solidification of Cu. In the sample $S_{Pb-S-0}$, the content of Pb is about 1.98 wt.% in interstitial phases and cannot be detected in silicate phases. However, the Pb content is about 1.10 wt.% in silicate phases and 3.65 wt.% in interstitial phases with the addition of 2 wt.% of sulfur as $CaSO_4 \cdot 2H_2O$ and $CaS$. About 0.26 wt.% and 2.1 wt.% of Cd were solidified in silicate phases.
phases and interstitial phases of $S_{Cd-S-0}$ sample, respectively. With the addition of CaSO$_4$·2H$_2$O and CaS, the solidified content of Cd in silicate and interstitial phases increased in about 35% and 18%, comparing to the $S_{Cd-S-0}$ sample. The results above confirmed the discussion in Section 3.1 and 3.4.1. For silicate phases of C$_2$S and C$_3$S, during clinkerization, the C$_3$S is formed by the combination of C$_2$S and free lime in the liquid phase. C$_3$S cannot massive formation before liquid phase appears. According to the discussion presented above, the addition of sulfur promoted the migration of heavy metals in the liquid phase, that intensified the ion substitution in C$_3$S and C$_2$S. Therefore, the incorporation content of Pb and Cd in silicate phases increased with the addition of CaSO$_4$·2H$_2$O and CaS. The mineralizing effects of CaSO$_4$·2H$_2$O and CaS for the samples added with Cu is not obvious due to good mineralizing effect.

**Table 2**

The average content of heavy metals in silicate and interstitial phases of clinker samples sintered at 1450°C (wt. %).

<table>
<thead>
<tr>
<th>ID.</th>
<th>Heavy metals in silicate phase</th>
<th>Heavy metals in interstitial phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Pb</td>
</tr>
<tr>
<td>$S_{Cu-S-0}$</td>
<td>0.40±0.13</td>
<td></td>
</tr>
<tr>
<td>$S_{Cu-CaSO4-2.0}$</td>
<td>0.37±0.10</td>
<td></td>
</tr>
<tr>
<td>$S_{Cu-CaS-2.0}$</td>
<td>0.38±0.12</td>
<td></td>
</tr>
<tr>
<td>$S_{Pb-S-0.0}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_{Pb-CaSO4-2.0}$</td>
<td>1.10±0.18</td>
<td></td>
</tr>
<tr>
<td>$S_{Pb-CaS-2.0}$</td>
<td>1.07±0.15</td>
<td></td>
</tr>
<tr>
<td>$S_{Cd-S-0.0}$</td>
<td></td>
<td>0.26±0.09</td>
</tr>
<tr>
<td>$S_{Cd-CaSO4-2.0}$</td>
<td>0.35±0.11</td>
<td></td>
</tr>
<tr>
<td>$S_{Cd-CaS-2.0}$</td>
<td>0.33±0.13</td>
<td></td>
</tr>
</tbody>
</table>

Note: -, undetected; ±, standard deviation.
3.5. Effects of sulfur on the chemical forms of Cu, Pb, and Cd

According to Herfort et al. [31], at low concentration, heavy metals enter into the structure of the initial phases of the clinker (C₃S, C₂S, C₃A and C₄AF) and form different phase assemblages of solid solutions. When the content of heavy metals increases, the presence of new phases might be observed. For example, the formation of Ca₂CuO₃ and CaCu₂O₃ were identified by XRD in the clinkers. The scanning electron microscopy images (backscattered electron imaging detector) of the clinker samples sintered at 1450°C (Figure 12) show that new phases were formed in the samples with the addition of CaSO₄·2H₂O. From the discussion in Section 3.4, sulfur promote Cu, Pb, and Cd solidification within interstitial phases forming solid solutions. During that process, the formed solid solutions not only contained heavy metals, but also contained S, that transformed the existence forms of heavy metals in the clinker. The variable compositions of the solid solutions in the interstitial phases were shown in Table 3.
**Fig. 12.** Scanning electron microscopy images with backscattered electron imaging of the mineral phases: a) $S_{\text{Cu-S-0}}$; b) $S_{\text{Cu-CaSO}_4-2.0}$; c) $S_{\text{Pb-S-0}}$; d) $S_{\text{Pb-CaSO}_4-2.0}$; e) $S_{\text{Cd-S-0}}$; f) $S_{\text{Cd-CaSO}_4-2.0}$.

**Table 3**

Clinker phase composition based on SEM/EDS analysis (wt.%) and empirical formula of solid solution.

<table>
<thead>
<tr>
<th>Cu-S-2%</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>Ca</th>
<th>Fe</th>
<th>Cu</th>
<th>Formula composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitial</td>
<td>38.6</td>
<td>3.8</td>
<td>10.1</td>
<td>5.6</td>
<td>35.8</td>
<td>4.1</td>
<td>2.1</td>
<td>$\text{Ca}<em>{1.85}\text{Fe}</em>{0.15}\text{Cu}<em>{0.07}\text{Al}</em>{0.25}\text{Si}<em>{0.75}\text{S}</em>{0.36}\text{O}_{5.00}$</td>
</tr>
<tr>
<td>phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interstitial</td>
<td>38.5</td>
<td>3.4</td>
<td>3.2</td>
<td>10.3</td>
<td>37.9</td>
<td>4.7</td>
<td>2.0</td>
<td>$\text{Ca}<em>{1.96}\text{Fe}</em>{0.17}\text{Cu}<em>{0.06}\text{Al}</em>{0.22}\text{Si}<em>{0.67}\text{O}</em>{5.00}$</td>
</tr>
<tr>
<td>phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interstitial</td>
<td>35.5</td>
<td>8.6</td>
<td>6.7</td>
<td>0.29</td>
<td>39.8</td>
<td>6.1</td>
<td>2.9</td>
<td>$\text{Ca}<em>{2.22}\text{Fe}</em>{0.25}\text{Cu}<em>{0.10}\text{Al}</em>{0.72}\text{Si}<em>{0.52}\text{S}</em>{0.02}\text{O}_{5.00}$</td>
</tr>
<tr>
<td>phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interstitial</td>
<td>40.7</td>
<td>2.0</td>
<td>6.4</td>
<td>10.8</td>
<td>37.9</td>
<td>1.7</td>
<td>0.58</td>
<td>$\text{Ca}<em>{1.86}\text{Fe}</em>{0.06}\text{Cu}<em>{0.02}\text{Al}</em>{0.14}\text{Si}<em>{0.45}\text{S}</em>{0.66}\text{O}_{5.00}$</td>
</tr>
<tr>
<td>phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interstitial</td>
<td>37.9</td>
<td>6.8</td>
<td>5.1</td>
<td>4.4</td>
<td>36.8</td>
<td>6.6</td>
<td>2.5</td>
<td>$\text{Ca}<em>{1.94}\text{Fe}</em>{0.25}\text{Cu}<em>{0.08}\text{Al}</em>{0.51}\text{Si}<em>{0.32}\text{S}</em>{0.29}\text{O}_{5.00}$</td>
</tr>
<tr>
<td>phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interstitial</td>
<td>37.8</td>
<td>5.9</td>
<td>2.9</td>
<td>7.8</td>
<td>36.4</td>
<td>6.0</td>
<td>3.2</td>
<td>$\text{Ca}<em>{1.92}\text{Fe}</em>{0.22}\text{Cu}<em>{0.11}\text{Al}</em>{0.46}\text{Si}<em>{0.22}\text{S}</em>{0.51}\text{O}_{5.00}$</td>
</tr>
<tr>
<td>phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interstitial</td>
<td>41.8</td>
<td>4.1</td>
<td>1.1</td>
<td>15.1</td>
<td>32.9</td>
<td>2.1</td>
<td>3.0</td>
<td>$\text{Ca}<em>{1.67}\text{Fe}</em>{0.07}\text{Cu}<em>{0.09}\text{Al}</em>{0.29}\text{Si}<em>{0.07}\text{S}</em>{0.90}\text{O}_{5.00}$</td>
</tr>
<tr>
<td>phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interstitial</td>
<td>37.1</td>
<td>8.8</td>
<td>1.8</td>
<td>4.9</td>
<td>32.9</td>
<td>11.6</td>
<td>3.1</td>
<td>$\text{Ca}<em>{1.77}\text{Fe}</em>{0.49}\text{Cu}<em>{0.10}\text{Al}</em>{0.76}\text{Si}<em>{0.14}\text{S}</em>{0.70}\text{O}_{5.00}$</td>
</tr>
<tr>
<td>phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interstitial</td>
<td>40.9</td>
<td>4.7</td>
<td>0.84</td>
<td>12.7</td>
<td>33.7</td>
<td>5.3</td>
<td>2.0</td>
<td>$\text{Ca}<em>{1.65}\text{Fe}</em>{0.18}\text{Cu}<em>{0.06}\text{Al}</em>{0.32}\text{Si}<em>{0.06}\text{S}</em>{0.87}\text{O}_{5.00}$</td>
</tr>
</tbody>
</table>
4. Conclusions

The effects of sulfur on the fate of Cu, Pb, and Cd during clinkerization were discussed in this work. The main conclusions can be summarized as follows:

- Sulfur promotes the volatilization of Pb and Cd at the temperature from 950°C to 1250°C by decreasing the melting point of PbO and CdO. The volatilization ratio of Cu increased due to its volatilization temperature decreased with sulfur addition at the temperature from 950°C to 1450°C. Sulfur decreased the volatilization temperature of CuO, PbO, and CdO for about 40°C, 65°C, and 35°C, respectively. Sulfur acts as a mineralizer/flux changing the thermodynamic stability of CuO/PbO/CdO and, therefore, lowering their volatilization temperature. Sulfur...
increased the solidification ability of clinker decreasing the volatilization ratio of Pb and Cd at the temperature of 1350-1450°C and 1450°C, respectively. Both forms of sulfur (CaSO₄·2H₂O and CaS) have similar effect on the Cu/Pb/Cd volatilization.

- Sulfur concentrated in interstitial phases of the clinkers mainly as Ca₄Al₆O₁₂SO₄ and CaSO₄.
- Cu, Pb and Cd were found to form solid solutions with the variable compositions within interstitial phases of the clinkers. Besides, crystalline phases of Ca₂CuO₃ and CaCu₂O₃ were identified in the clinkers.

However, the effect of sulfur on the volatilization of Cu, Pb, and Cd might be different, if those metals present together in the system (e.g., solid wastes) due to their possible competitive effects. Therefore, further investigation of the element fate during clinkerization in multi-elemental system is required.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (NSFC, No. 5141101056) and Guangdong science and Technology Department (2014B020216002).

References


